

Extension of structure integration to magnetic system

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We extend our previously developed method, "structure integration", to evaluate free energy directly for magnetic large systems on given lattice. The present method express the density of states(DOS) as the parameters independent of system but depend on lattice, and replace the DOS unknown *a priori* as that known *a priori*. Through two-dimensional square lattice Ising model, we find that the present method can evaluate magnetic free energy efficiently and accurately above critical temperature without iterative method like Monte Carlo simulation.

I. INTRODUCTION

Helmholtz free energy, F , is the most important and essential property in thermodynamics. In statistical mechanics, however, estimating Helmholtz free energy is a challenging problem, because F is not statistically averaged value that is easily obtained by Metropolis algorithm¹. F is derived from partition function, Z , that is defined by:

$$Z = \sum_E W(E) \exp\left(-\frac{E}{k_B T}\right), \quad (1)$$

where W is the number of states, k_B is boltzmann constant and E is total energy. Here $W(E)$ is needed to obtain Z , however $W(E)$ is not known *a priori*. The most simple approach to obtain $W(E)$ is to search phase space and calculate E for all possible states. This approach requires enormous computational cost, therefore this approach is limited for small system because of practical difficulty. Microscopic structure of substitutional crystalline solids is often represented by Ising Hamiltonian, where phase space can be splitted into momentum space and configuration space². In order to estimate Z on Ising Hamiltonian for large system, two main methods exist; (i) analytical methods and (ii) numerical methods. In (i), for example, transfer-matrix method³ is one of the most successful method to give exact solution of free energy. However, since such analytical methods are limited to the system whose Hamiltonian is quite simple, analytical methods cannot be applied to the system whose Hamiltonian has multibody interaction terms. This difficulty can be avoided using (ii) such as multicanonical ensemble⁴⁻⁶, entropic sampling⁷, Wang-Landau method^{8,9} and so on. Although these method effectively sample microscopic states over vast configuration space, these methods cannot avoid the problem with computational cost that increase in system size. This is because the number of points in configuration space exponentially increase with increase of system size(e.g., in N spin Ising model, the number of points in configuration space is 2^N). In addition, as the number of interactions increase, problems become too intractable. As shown in (i) and (ii), estimating Z suffers from increasing both N and the number of interactions.

We have recently proposed a new approach, "structure integration(SI)"¹⁰, overcoming above difficulties and enabling direct evaluation of configurational free energy for large binary alloy system. SI gives universal and analytical representation of W via so-called "correlation functions"¹¹ which does not depend on both constituent elements or system size. Since SI is based on information about density of microscopic states on configuration space established from crystal lattice¹², SI can be applied to any lattice system, e.g., fcc, bcc, hcp and square lattice with any number of multibody interactions. In our previous study¹⁰, we applied SI to equiatomic Cu-Au alloy, that show first order phase transition from $L1_0$ to disorder states above critical temperature, T_c , through first-principles-based simulation. Comparing with free energy using SI and exact method in small system, we found that SI could evaluate configurational free energy accurately in disorder states above T_c . This good agreement for disorder states implies that our analytical representation of W can describe the major part of true W . However, since SI have been established based on "constant" composition, analytical representation of W could not be applied for the system where composition can vary.

In present study, we give an analytical representation of W for any composition and extend SI to magnetic system. This extension enable us to estimate Z in large spin system for multibody interactions. In order to confirm validity and applicability, we apply the present method to a model system, two-dimensional(2D) square lattice Ising model that has been generally used as a benchmark for new simulation, because spin system cannot be described by equicomponent method.

II. METHODOLOGY

In this section, first, we give a brief explanation of SI and generalized Ising model. Second, the derivation of extension of SI to magnetic system is shown. Finally, we show how the extended SI is applied to a simple model system.

A. Structure integration approach

In order to describe thermodynamic property via microscopic states confined to atomic arrangements on a given lattice, generalized Ising model for multibody interactions¹¹ has been proposed and widely used in alloy studies. Then, configurational property, e.g., E , is completely represented via correlation functions, ξ_k ,

$$E = \sum_k V_k \xi_k, \quad (2)$$

where k and V_k denote the figure of cluster (e.g., point, pair, triangle and tetra) and effective cluster interaction (ECI). ξ s are product of complete basis function that are constructed by Gram-Schmidt orthonormalization. Especially in binary alloy system, the basis functions are $\{1, \theta\}$ where θ is a spin variable that has +1 or -1. Therefore in binary case, ξ_k are expressed by the average for spin products in cluster k . From the completeness and orthogonality of ξ s, V_i is described by $\langle E | \xi_i \rangle$, where $\langle | \rangle$ denotes inner product. This means that the configurational property can be split into the term depend only on lattice and on others. In our previous study¹², we confirmed that the distribution of any ξ_k numerically obey to normal distribution function (NDF) at large system size, $P_k(\xi_k)$, whose average, μ_k , and standard deviation, σ_k , are as follows¹³:

$$\mu_k = (2x - 1)^k, \quad (3)$$

$$\sigma_k = \frac{1}{\sqrt{ND_k}} \quad (x = 0.5). \quad (4)$$

Here x is composition, N is the number of sites and D_k is the number of k clusters per site. In upper part of Fig. 1, we compare the distribution from Monte Carlo (MC) simulation and the DOS known *a priori*. This good agreement is reliable in disorder states. We confirmed that any single variable $P_k(\xi_k)$ correspond to marginal distribution of the DOS in terms of the set of ξ s, $\tilde{\xi}$.^{10,12} In SI, we approximate that any correlation coefficient between different ξ s are zero at thermodynamic limit, i.e.,¹²

$$P(\tilde{\xi}) \simeq \prod_k P_k(\xi_k). \quad (5)$$

From Eq. (1), (2) and (5), Z is rewritten as¹⁰

$$Z \simeq \prod_k \int P_k(\xi_k) \exp\left(-\frac{V_k \xi_k}{k_B T}\right) d\xi_k. \quad (6)$$

We call Eq. (6) "structure integration" because the integration variable means the basis of configuration. Although ξ_k is discrete variable, in Eq. (6) we employ integral instead of sum, because expressing the DOS as Eq. (5) is allowed at thermodynamic limit. Eq. (6) can be applied only to equicomponent alloy, because Eq. (4) holds only for equiatomic composition. Therefore, SI cannot be applied to magnetic system.

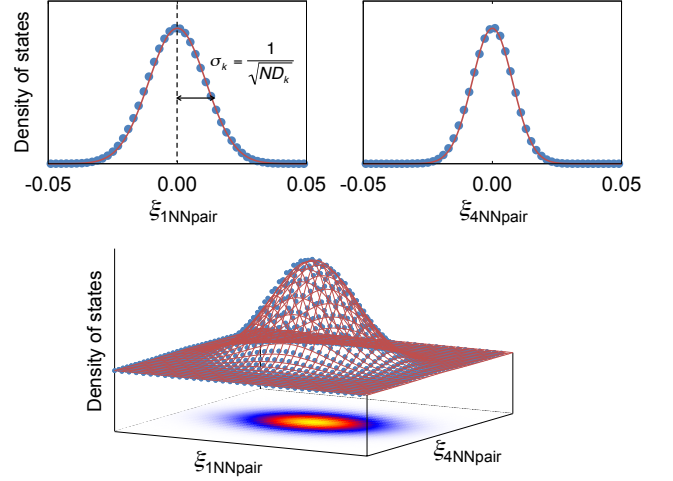


FIG. 1. Upper part: Density of states in terms of correlation function. Points denote the normalized number of states from MC simulation in $A_{2048}B_{2048}$ binary alloy system on 2D square lattice. Solid curves are normal distribution function whose average and standard deviation are derived from lattice. Lower part: Density of states in SI for $E = \sum_k V_k \xi_k$ where k means the first and fourth nearest neighbor pair (1NNpair and 4NNpair) cluster.

B. Present extension of structure integration

Here we extend Eq. (6) to any composition. When the changes in composition is included to Z , $P_k(\xi_k)$ and intervals of integration should be rewritten to be in terms of x . The characteristics of $P_k(\xi_k)$ are determined by μ_k and σ_k .

For simplicity and correspondence to Ising model, without the lack of generality, hereinafter we consider $E = V\xi$ where $\xi = \sum_{\langle i,j \rangle} \theta_i \theta_j$ and $\langle i,j \rangle$ denotes that a pair of θ_i and θ_j is nearest neighbor, i.e., E is expressed by single correlation function. In Ising model, Z is derived from the sum of boltzmann factor, $\exp(-V\xi/k_B T)$, over all possible configuration. Meanwhile in SI, since configuration space is expressed as (x, ξ) , the DOS should be expressed in terms of x and ξ ; $P(x, \xi)$. From previous study¹⁰, we know that $P(0.5, \xi)$ is described by NDF of which average and standard deviation are Eq. (3) and (4), and we also have shown that $P(x, \xi)$ where $x \neq 0.5$ can also be described by NDF in large system size.

Since μ_k in Eq. (3) is already described by x , σ_k should be described in terms of x . Through MC simulation for $N = 2048$ atoms on fcc lattice with $A_x B_{1-x}$ binary system, $\sigma_k(x)$ for each x is shown in Fig. 2. In Fig. 2, we find that the points denote the standard deviations are well described as:

$$\sigma_k(x) \simeq \frac{1 - 4(0.5 - x)^2}{\sqrt{ND_k}}. \quad (7)$$

Eq. (7) satisfies the conditions that $\sigma_k(0) = 0$, $\sigma_k(0.5) = \sqrt{ND_k}$ and $\sigma_k(1) = 0$. We also confirm that

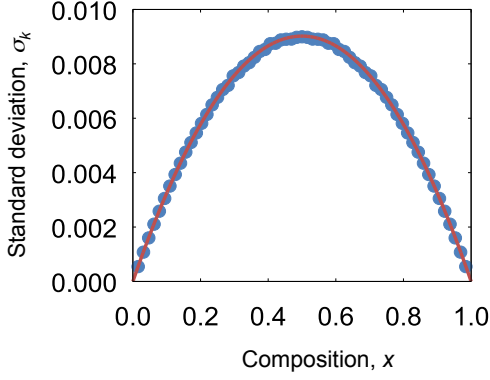


FIG. 2. Standard deviation as a function of composition in A_xB_{1-x} binary alloy system on fcc lattice when $8 \times 8 \times 8$ supercell. Points and solid curve denote the result of MC simulation and fitted quadratic function (Eq. (7)).

Eq. (7) is satisfied on 2D square lattice. The form of $P(x, \xi)$ for each x is shown, and furthermore we should consider the total number of states for each x . The total number of states is ${}_NC_{Nx}$, and this should be described by the gamma function as ${}_NC_{Nx} = \Gamma(N+1)/\Gamma(Nx+1)\Gamma(N(1-x)+1)$ in the SI formalism in order to employ integration. Using Eq. (7) and the gamma function, $P(x, \xi)$ is described as:

$$P(x, \xi) \simeq \frac{1}{\sqrt{2\pi\sigma(x)^2}} \frac{\Gamma(N+1)}{\Gamma(Nx+1)\Gamma(N(1-x)+1)} \times \exp\left(-\frac{(\xi - \langle \xi \rangle)^2}{2\sigma(x)^2}\right). \quad (8)$$

Then Z is rewritten as:

$$Z \simeq \int_x \int_{\xi} P(x, \xi) \exp\left(-\frac{V\xi}{k_B T}\right) d\xi dx. \quad (9)$$

An advantage of this new expression of Z is that the computational cost does not depend on N , because x and ξ are intensive variables. In contrast, additivity of F is explicitly considered in $P(x, \xi)$ and V . Since Z is analytically rewritten, our method does not need iterative method like MC simulation. When the number of V_k is more than one, Eq. (9) becomes:

$$Z \simeq \int_x \prod_k \int_{\xi_k} P_k(x, \xi_k) \exp\left(-\frac{V_k \xi_k}{k_B T}\right) d\xi_k dx.$$

Here approximately equal is caused by Eq. (5). As above, we emphasize that our method can be applied to any lattice and any number of interactions. Note that SI cannot be applied if any correlation coefficient between different ξ s does not approach to zero at thermodynamic limit. We confirmed that when constituent lattice points on cluster k are all included in those on cluster k' , the correlation coefficient between k and k' does not approach to zero at thermodynamic limit. In our previous study¹⁰, we

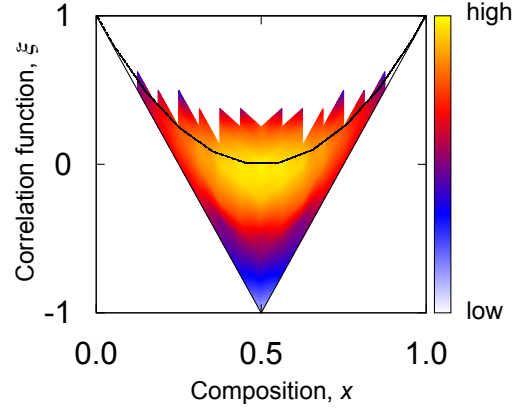


FIG. 3. The number of all possible states in terms of x and ξ in 4×4 2D square lattice Ising model. An open triangle and a quadratic curve denote the expected limitation for x and ξ at thermodynamic limit and μ_k in Eq. (3).

showed that this difficulty can be overcome using a new basis set that makes any non zero correlation coefficients between different ξ s zero.

III. RESULT AND DISCUSSION

In order to calculate Eq. (9), intervals of integration should be determined as in terms of ξ_k . In our previous study in CuAu¹⁰, we determined the intervals of integration as $-3\sigma_k < \xi_k < -3\sigma_k$ for any k . This is because $P(\vec{\xi})$ obeys to multivariate NDF. Meanwhile, in this study, we choose a model system, 2D square lattice Ising model that does not have geometrical frustration and whose configurational polyhedron¹⁴ can be easily obtained. In 4×4 square lattice Ising model, the exact DOS in terms of x and ξ is obtained through counting all possible states, and is shown in Fig. 3. As shown in Fig. 3, we can easily estimate the intervals of integration at thermodynamic limit. The upper limit of ξ increase toward to +1 with the increase of N , and the lower limit of ξ is estimated as follows:

$$\xi = \begin{cases} 1 - 4x & (0 \leq x \leq 0.5) \\ 4x - 3 & (0.5 < x \leq 1) \end{cases}$$

We show these limitation of ξ s in Fig. 3 as straight black lines, and also show Eq. (3) as a quadratic curve. These limitations of ξ s are chosen in this study.

Since free energy estimated by SI does not depend on system size, for practical use, we can employ SI for any finite system size, which should always give identical result at thermodynamic limit. However, suppose the fact that the DOS in terms of ξ numerically obey to NDF is valid at thermodynamic limit, it is natural to employ SI in large system size. Using SI, We obtained free energies in the $L \times L$ Ising square lattice for each $L = 16, 32, 64$ and

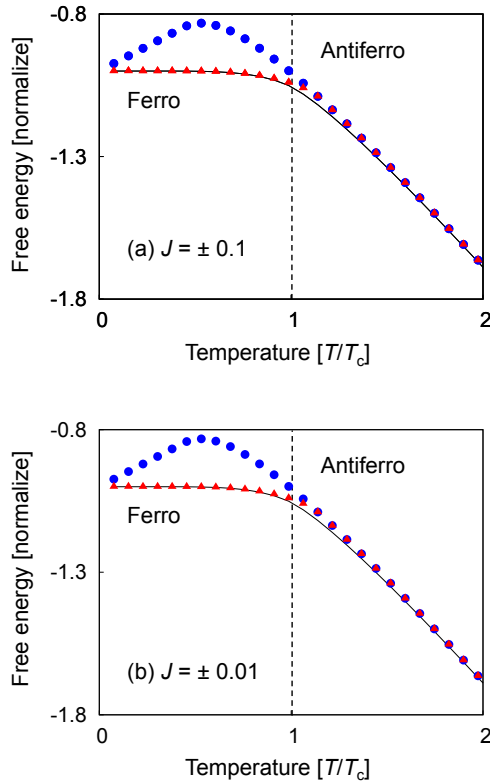


FIG. 4. Free energy 2D square lattice Ising model where (a) $J = \pm 0.1$ and (b) $J = \pm 0.01$. Solid line and points denote exact solution and the result using our method in 128×128 square lattice for ferro and anti ferro magnetism.

128 with nearest neighbor coupling constants $J = \pm 0.01$ where $J > 0$ and $J < 0$ correspond to antiferro and ferro magnetism, and confirmed the converged result in $L = 128$.

In Fig. 4, free energy via exact and our method are shown where (a) $J = \pm 0.1$ and (b) $J = \pm 0.01$. Here we use a normalized unit that F is divided by J because Fig. 4 clearly shows that changes in J make no difference to the normalized F . Note that exact result is symmetric for J but our results are not. This is because the DOS in terms of x and ξ is symmetric for μ , and μ is absolute value when the number atoms in cluster k is even (see Eq. (3)). Fig. 4 shows that above T_c , SI evaluate magnetic free energy accurately for both ferro and anti-ferro magnetism. This accurate prediction of F above T_c has the same tendency for alloy system with constant composition, which has been confirmed by our previous study¹⁰. In particular for ferro magnetism system, SI successfully reproduces the free energy not only above T_c but also under T_c . This means that our *a priori* known DOS efficiently describe the tendency that all spins are up or down and disorder.

IV. SUMMARY

We propose an extended method to estimate configurational free energy directly for any composition, lattice, and the number of interactions. The new expression of Z in Eq. (9) that known *a priori* is valid for 2D square lattice Ising model above critical temperature.

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